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Synthesis and Characterization of Pd^{II} Complexes with Bis-Pyridinium and Isoquinolinium N-Ylides: Moderate C—H···O═C Intramolecular Hydrogen Bonds as Source of Conformational Preferences

Agustí Lledós,*,[†] Jorge J. Carbó,[†] Rafael Navarro,[‡] Elena Serrano,[‡] and Esteban P. Urriolabeitia*,[‡]

Departament de Química, Edifici C.n., Universitat Autònoma de Barcelona,
08193 Bellaterra, Barcelona, Spain, and Departamento de Química Inorgánica, Instituto de
Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., Plaza de San Francisco s/n,
E-50009 Zaragoza, Spain

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The bis(N-ylide) Pd^{II} complexes *cis*-$[PdX_2\{\eta^2\text{-}[C(H)NC_xH_y]_2CO\}]$ (X = I, $NC_xH_y = NC_5H_5$, **2a**; X = Br, NC_xH_y = NC_5H_5 and NC_5H_3-2,3-Me_2, **2c**, isoquinolinium NC_9H_7, **2d**) have been prepared by reaction of the corresponding bis-pyridinium salts with $Pd(OAc)_2$ (1:1 molar ratio). Compounds **2** react with $AgClO_4$ and Tl(acac) (1:1:1 molar ratio) to give the acetylacetonato derivatives $[Pd(acac\text{-}O,O')\{\eta^2\text{-}[C(H)NC_xH_y]_2CO\}]ClO_4$ (**3a, c, d)**. In compounds **2** and **3**, the bis-ylide is bonded as a C,C-chelate ligand through the two ylidic C_α atoms. The reaction is stereoselective, and only one diastereoisomer is observed (meso form, RS/SR). The origin of the observed stereoselectivity lies with the establishment of intramolecular C—H···O═C hydrogen bonds between the ortho protons of the pyridine or isoquinoline fragments and the carbonyl oxygen, as it has been shown by density functional theory (DFT) calculations (B3LYP level) and Bader analysis of the electron density on model pyridinium ylides. Despite the inherent weakness of the C—H···O═C bonds, the results show that in these N-ylides the hydrogen bonds are stronger than expected and should be classified as moderate H bonds.

Introduction

We have recently shown[1] that the presence of intramolecular contacts 1,4-P···O in α-stabilized ylides $[Ph_3P{=}C(H)C(O)R]$ or the bis-ylide $[Ph_3P{=}C(H)C(O)C(H){=}PPh_3]$ results in strong conformational preferences favoring the cisoid conformation. Moreover, we have shown that these preferences are responsible for the stereoselective bonding of the bis-ylide to the $PdCl_2$ unit, yielding a single diastereoisomer $[PdCl_2\{\eta^2\text{-}[C(H)PPh_3]_2CO\}]$ (RS/SR, meso form).[2] These facts are good examples of how weak, nonbonding contacts could determine the stereochemistry of a given process.

Following this, and as part of our current research in α-stabilized ylides, we have now focused our attention on pyridinium N-bis-ylides $[H_yC_xN-C(H)C(O)C(H)-NC_xH_y]$. Our purpose is the study of their bonding properties, the plausible presence of similar conformational preferences as those shown by the P-ylides, and the source of these preferences. At first sight, it seems likely that N···O interactions could play a role in N-ylides, the same role as the P···O contacts in P-ylide complexes (Figure 1).

The presence of short N···O contacts in pyridinium-based structures is a well-known fact, and it has been studied, for instance, in neutral pyridinium betaines,[3] in the synthesis of self-assembly motifs based on crown ethers and pyridinium compounds,[4] and in cationic pyridinium salts.[5] The neutral betaines[3] and cationic salts[5] show N···O intramolecular contacts of Coulombic nature, as shown by theoretical calculations,[3d] but for inclusion compounds[4] more interactions must be considered (H bonding, π-stacking) although the electrostatic N···O interactions are the main contribution to the bonding.[4a,f]

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* Authors to whom correspondence should be addressed. E-mail: esteban@unizar.es; agusti@klingon.uab.es.

[†] Universitat Autònoma de Barcelona.

[‡] Universidad de Zaragoza-C.S.I.C.

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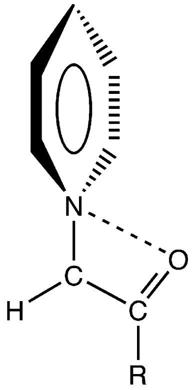
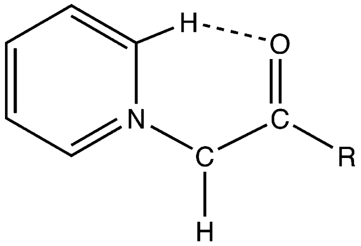


(a): 1,4-N···O interaction



(b): 1,6-CH···O H-bond

Figure 1.

However, in the case of pyridinium ylides, a search in the Cambridge Crystallographic Data Center database[6] shows that two different situations must be considered (Table 1), (i) nonplanar (entries 1−8) and (ii) planar molecules (entries 9−15). The nonplanar ylides[7] show intramolecular $N\cdots O$ distances ranging from 2.50 to 3.00 Å and torsion angles $NC_{\alpha}C_{\beta}O$ [T(NCCO)] and $C_{ortho}NC_{\alpha}C_{\beta}$ [T(CNCC)] ranging from 0 to 17° and from 66 to 90°, respectively, the latter being a clear indication of their deviation from the planarity. The planar ylides[8] show long $N\cdots O$ distances (2.88−3.27 Å) and the torsion angles T(NCCO) and T(CNCC) show values near to 0°. Although in the nonplanar ylides, the $N\cdots O$ distance is shorter than the sum of the van der Waals radii (3.02 Å),[9] suggesting the presence of $N\cdots O$ contacts; in the planar ylides, the $N\cdots O$ distance is only slightly shorter or even higher than this value. In addition, the planar disposition and the cisoid arrangement of the NCCO skeleton preclude an optimal interaction between the N and O atoms. A careful inspection of the planar structures shows that, in all cases, a possible intramolecular H bond can be established between the H_{ortho} proton of the pyridine ring and one oxygen atom of the stabilizing groups (see Figure 1). The characterization of these H bonds[10a] is shown in Table 1. The $O\cdots H$ distances range from 2.10 to 2.44 Å, the $O\cdots C$ distances from 2.78 to 3.20 Å, and the $C-H\cdots O$ angles from 118 to 138°. Usually, the $C-H\cdots O$ bond is, by far, the prototype of a weak hydrogen bond,[10] although the strong end of the interaction has not yet been well explored. Very recently some examples of strong $C-H\cdots O$ bonds have been reported.[10n,o]

Aiming to shed light in all these questions, we have prepared and fully characterized several Pd^{II} complexes with pyridinium and isoquinolinium N-bis-ylides $[H_yC_xN-C(H)C(O)C(H)-NC_xH_y]$. In all studied cases, we have found a C,C-bonding of the bis-ylides which results in the selective synthesis of the meso diastereoisomers $[PdX_2\{\eta^2$-[C(H)-

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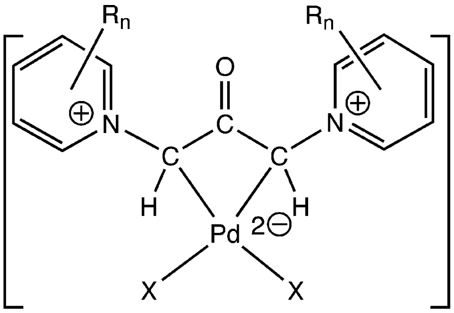
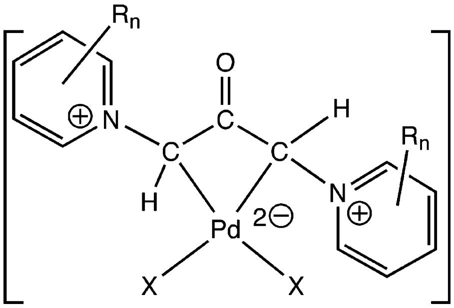
Table 1. Different Structural Motifs Found in Pyridinium Ylides

CCDC ref	*d*(N···O)	*T*(NCCO)	*T*(CNCC)	*d*(O···H)	*d*(O···C)	α(O···H−C)	ref
ACROEY	2.820	4.8	102.9				7a
CEYWEI	2.642	−3.0	78.8				7b
	2.671	8.3	66.0				
CEYWIM	2.565	−5.1	−90.1				7b
	2.548	3.1	−74.9				
FALPAJ	2.735	0.00	−87.3				7c
JIBGUW	2.696	16.9	67.8				7d
MAPGIT	2.749	−2.5	72.8				7e
PBMTXE	2.937	−6.8	86.4				7f
VOBHAV	3.004	5.4	−70.5				7g
BCAIMP	2.898	−3.7	5.3	2.356	2.926	129.8	8a
BERMYA	2.905	−7.1	−4.3	2.132	2.811	126.5	8b
GEKDUV	2.909	−0.4	10.7	2.132	2.781	122.3	8c
POZWUW	2.877	4.6	−2.7	2.308	2.887	118.7	8d
PYINDB	3.062	2.3	3.0	2.106	2.882	137.5	8e
	3.053	1.5	4.2	2.117	2.872	137.7	
QIHPUS	3.249	2.7	−4.0	2.434	3.171	132.8	8f
	3.270	−1.7	0.2	2.438	3.203	138.5	
QIZLAM	2.882	−6.5	12.0	2.304	2.878	119.5	8g



(a): *meso* form (*RS*/*SR*)



(b): *d,l* form (*RR*/*SS*)

Figure 2.

$NC_xH_y]_2CO\}]$ (RS/SR) although two different diastereosiomers are envisageable (Figure 2). This fact suggests the presence of strong conformational preferences on the free bis-ylides. The density functional theory (DFT) study (at the B3LYP level)[11] of several α-stabilized ylides $[H_5C_5N-C(H)C(O)R]$, the bis-ylide $[H_5C_5N-C(H)C(O)C(H)-NC_5H_5]$, and the complex $[PdI_2\{\eta^2\text{-}[C(H)NC_5H_5]_2CO\}]$ has shown that the preferred arrangement in these ylides is planar and cisoid at the $NC_\alpha C_\beta O$ skeleton and that the source of the observed preferences is the presence of C−H···O=C hydrogen bonds much stronger than usual, which can be classified as moderate following the classification of Jeffrey.[10l,m]

Results and Discussion

1. Synthesis of Bis-Ylide Complexes. The bis-pyridinium salt $[H_5C_5N-CH_2-C(O)-CH_2-NC_5H_5]I_2$ (**1a**) has been prepared according to literature methods (the Ortoleva−King process)[12] by reaction of acetone with elemental iodine in dry pyridine (Scheme 1). Attemps to obtain similar pyridinium salts derived from 2,3-lutidine or 2,6-lutidine afforded very complex mixtures of products. The reaction of an excess of 2,3-lutidine with 1,3-dibromoacetone $(BrCH_2)_2CO$ (10:1 molar ratio) in dry toluene at 25 °C gives the pyridinium salt $[2,3\text{-}Me_2C_5H_3N-CH_2C(O)CH_2Br]Br$ (**1b**). An increase in the temperature, using the same molar ratio but in different solvents, produces substantial decomposition and untractable oils. However, an increase in the molar ratio lutidine/ketone (at room temperature) did not afford the bis-derivative, and similar conversions of **1b** were obtained. Probably, this lack of reactivity could be related to the steric hindrance exerted by the two methyl groups, because the reaction of **1b** with a large excess of pyridine (40:1 molar ratio) in refluxing tetrahydrofuran (THF) affords cleanly the mixed salt $[2,3\text{-}Me_2C_5H_3N-CH_2C(O)CH_2-NC_5H_5]Br_2$ (**1c**) in good yields (Scheme 1). The reaction of a large excess of isoquinoline with 1,3-dibromoacetone (40:1 molar ratio) in toluene at 25 °C gives the bis(isoquinolinium) derivative $[H_7C_9N-CH_2C(O)CH_2-NC_9H_7]Br_2$ **(1d)** as an orange solid in quantitative yield. All these compounds were characterized through their analytic and spectroscopic data (see Experimental Section). Full assignment of all ^1H NMR resonances

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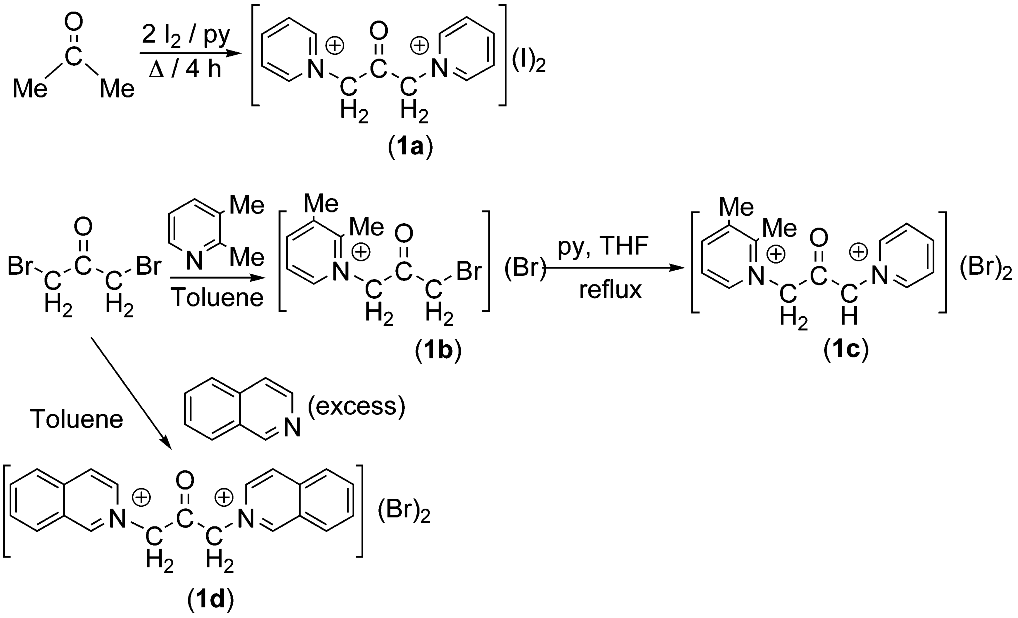
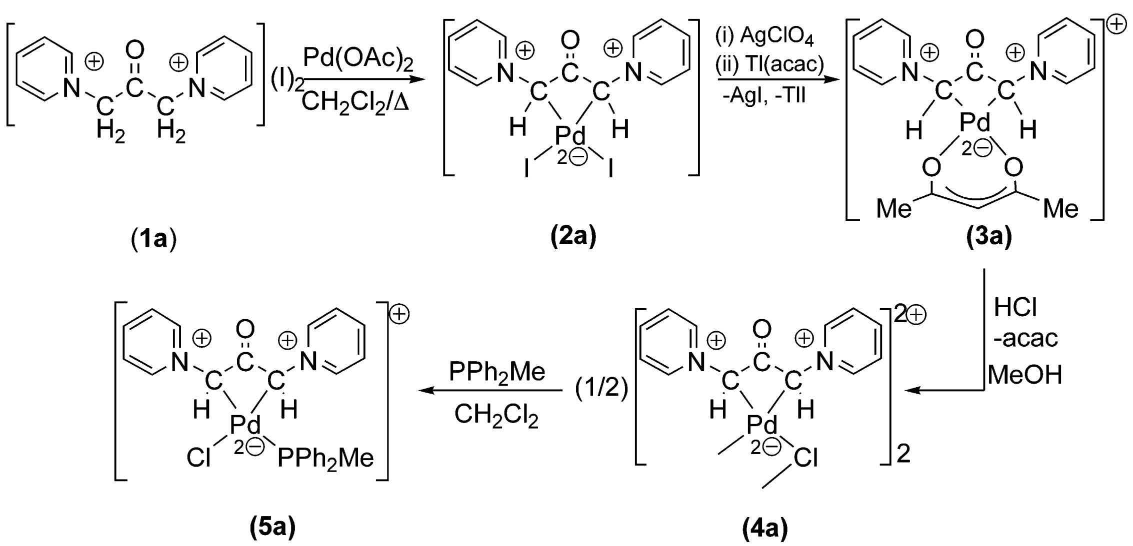
Scheme 1



Scheme 2



was performed with the help of two-dimensional (2D) $^1H-^1H$ correlation spectroscopy (COSY) experiments and by using selective 1D nuclear Overhauser enhancement spectroscopy (NOESY) and 1D rotational nuclear Overhauser effect spectroscopy (ROESY) sequences. Full assignment of all $^{13}C\{^1H\}$ NMR resonances was performed with the help of 2D $^1H-^{13}C$ heteronuclear single quantum correlation (HSQC) experiments. This applies not only for salts **1** but also for complexes **2**−**5**.

The reaction of the bis-pyridinium salt **1a** with $Pd(OAc)_2$ (OAc = acetate) in refluxing CH_2Cl_2 affords the C,C-chelate complex *cis*-$[PdI_2\{\eta^2\text{-}[CH(NC_5H_5)]_2C(O)\}]$ (**2a**) (Scheme 2) in nearly quantitative yield. In the same way, the reactions of the bis-pyridinium **1c** or the bis-isoquinolinium **1d** salts give (under the same experimental conditions) the C,C-chelate complexes *cis*-$[PdBr_2\{\eta^2\text{-}[2,3\text{-}Me_2-C_5H_3N-CHC(O)CH-NC_5H_5]\}]$ (**2c**) or *cis*-$[PdBr_2\{\eta^2\text{-}[CH(NC_9H_7)]_2C(O)\}]$ (**2d**) (Scheme 3). The structures shown in Schemes 2 and 3 for metallic complexes are proposed on the basis of (i) their spectroscopic parameters and (ii) very closely related processes.[13,14]

The IR spectra of **2a,c,d** show strong absorptions at about 1590 cm^{-1}, attributed to the ν_{CO} stretch, which are shifted to lower energies with respect to their respective positions in the starting pyridinium salts **1a,c,d** (about 1730−1750 cm^{-1}). Similar low-energy shifts have been found in the C,C-chelation of the bis-ylide $[Ph_3P{=}C(H)]_2C(O)$ to Pd^{II} [13] and also in the reaction of 1,3-bis(1-methylimidazolium-3-yl)-propan-2-one diiodide with $Pd(OAc)_2$.[14] In the first case, the ν_{CO} stretch varies from 1712 cm^{-1} in $[Ph_3PCH_2C(O)CH_2PPh_3]Cl_2$ to 1587 cm^{-1} in *cis*-$PdCl_2\{\eta^2\text{-}[C(H)PPh_3]_2CO\}$,[13] but in the second case, the ν_{CO} varies from 1749 cm^{-1} in

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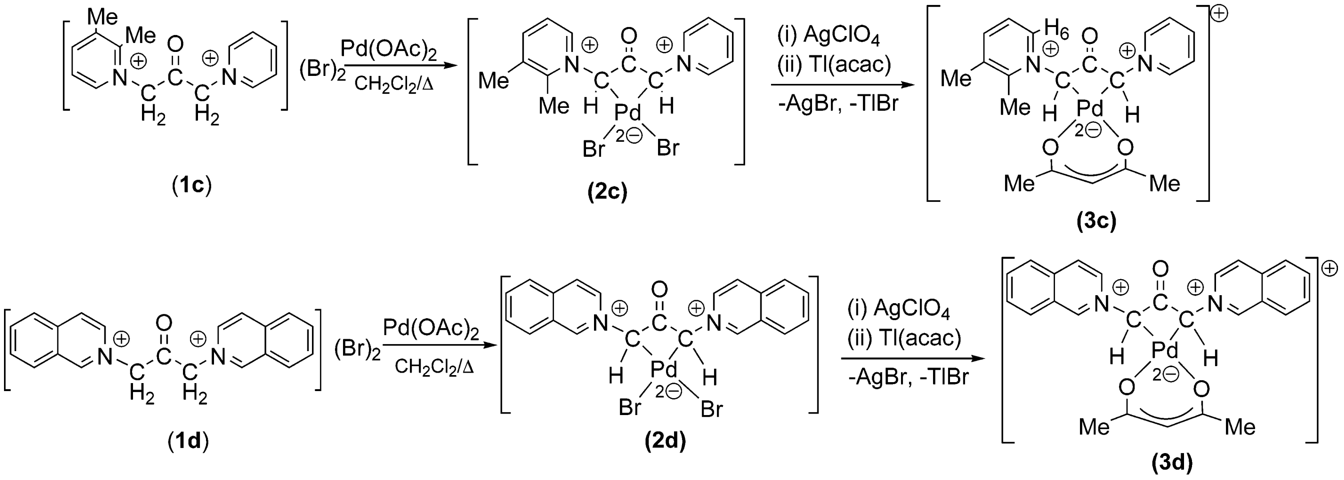
Scheme 3



the bis(imidazolium) salt to 1585 and 1564 cm^{-1} in *cis*-PdI$_2$-[η^3-{CH(MeIm)}$_2$CO].[14] These facts strongly suggest the C,C-bonding of the pyridinium bis-ylide in **2a,c,d**. Additional structural information can be inferred from the analysis of the NMR spectra of **2a,c,d**.

The ^{1}H NMR spectrum of **2a** displays a unique set of signals, showing the presence of a single reaction product and, moreover, of a single diastereoisomer. As a result of the C,C-bonding of the bis-ylide, several diastereoisomers are envisageable. From them, we can discard all possesing a planar PdC$_3$O core because it is well established that the C═O group never arranges coplanar with the Pd(C$_\alpha$)$_2$ unit in this type of bis-ylide complexes, regardless if the heteroatom is phosphorus (P-ylides)[13] or nitrogen (N-ylides).[14] For nonplanar structures with a PdC$_3$O, core we have two different diastereoisomers, the meso form (RS/SR configurations at the C$_\alpha$ atoms) and the d,l form RR/SS. In the aromatic region only three signals (relative intensity 2:1:2) are observed, showing the equivalence of the two pyridinic rings, which are able to freely rotate around the N−C$_\alpha$ bond. The equivalence of the two NC$_5$H$_5$ rings must be due to the presence of a symmetry plane, normal to the coordination plane, which contains the carbonyl group and the Pd atom. Our previous experience with P-ylides indicates that equivalence of the two halves of the molecule due to a C_2-symmetry axis generated by rapid change of the CO position is an unlikely process.[13] This fact clearly indicates that the configurations at the C$_\alpha$ atoms should be (RS/SR), that is, the meso form. We have depicted the structure of **2a** with the two pyridinium rings in pseudoequatorial positions because this is the less sterically hindered arrangement. The equivalence of the two halves of the molecule is also inferred from the observance in the ^{1}H NMR spectrum of only one signal for the ylidic proton, which appears at 5.84 ppm. The ^{13}C{^{1}H} NMR spectrum (attached proton test) of **2a** shows similar features. Only one signal was observed for the ylidic C$_\alpha$ atom, and only one set of resonances was observed for the pyridinic carbon atoms. Similar structural conclusions can be derived from the analysis of the NMR spectra of the bis-isoquinolinium complex **2d**. It is worthy of note that the meso form has also been found in the *cis*-PdI$_2$[η^3-{CH(MeIm)}$_2$CO] derivative.[14] In addition, the observed values for the chemical shifts of the C-bonded bis-ylide in **2a,d** are in good agreement with those previously reported for related Pd^{II} complexes with C-bonded pyridinium ylides.[15] In accord with all these facts, we propose the structures depicted in Schemes 2 and 3 for complexes **2a** and **2d**. In the case of complex **2c**, only one set of signals is observed, showing also the presence of a single product. However, because of the asymmetry of the bis-ylide ligand, both conformations (Figure 2, meso and d,l) could explain the observed data. The close appearance of the chemical shifts of the two ylidic protons precludes a proper measurement of the nuclear Overhauser effect (NOE) interactions between these two protons, even using soft selective gradient pulses. Further derivatization of **2a,c,d** was carried out.

The treatment of **2a,c,d** with AgClO$_4$ and Tl(acac) (acac = acetylacetonate) (1:1:1 molar ratio) gives the O,O′-acac derivatives [Pd(acac-O,O′){η^2-[C(H)NC$_x$H$_y$]$_2$CO}]ClO$_4$ (NC$_x$H$_y$ = NC$_5$H$_5$, **3a**; NC$_x$H$_y$ = NC$_5$H$_5$ and NC$_5$H$_3$-2,3-Me$_2$, **3c**, isoquinolinium NC$_9$H$_7$, **3d**) (see Experimental Section and Schemes 2 and 3) as soluble yellow solids. Attempts to isolate the μ-halide intermediates failed because of their insolubility in the reaction medium (mixture CH$_2$Cl$_2$/acetone 9:1) and the difficulty to separate them from the silver halide. For this reason, we have performed the synthesis of the acac derivatives in a one-pot reaction. The synthesis of the dinuclear μ-chloride derivatives can been performed successfully by simple treatment of the acac complexes **3** with HCl. Thus, treatment of the acac derivative **3a** with a methanolic solution of HCl (1:1 molar ratio) gives the dicationic complex [Pd(μ-Cl){η^2-[C(H)NC$_5$H$_5$]$_2$CO}]$_2$(ClO$_4$)$_2$ (**4a**), which shows the typical reactivity of this type of complex. For instance, the reaction of **4a** with 2 equiv of PPh$_2$Me produces the chloride bridge cleavage and gives the mononuclear derivative [Pd{η^2-[C(H)NC$_5$H$_5$]$_2$CO}(Cl)-(PPh$_2$Me)](ClO$_4$) (**5a**) (see Scheme 2).

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[15] (a) Koezuka, H.; Matsubayashi, G.-E.; Tanaka, T. *Inorg. Chem.* **1976**, *15*, 417. (b) Koezuka, H.; Matsubayashi, G.-E.; Tanaka, T. *Inorg. Chem.* **1975**, *14*, 253. (c) Fronza, G.; Bravo, P.; Ticozzi, C. *J. Organomet. Chem.* **1978**, *157*, 299. (d) Matsubayashi, G.-E.; Kondo, Y. *J. Organomet. Chem.* **1981**, *219*, 269.

Table 2. Bond Distances (Å) and Angles (deg) for Compounds **2** and **6**−**11**

	Bond Distances					Bond Angles			
	N−C$_\alpha$	C$_\alpha$−C$_\beta$	C$_\beta$=O	O···H	O···C	O···H−C	NC$_\alpha$C$_\beta$	C$_\alpha$C$_\beta$O	NC$_\alpha$C$_\beta$O
6cc	1.370	1.439	1.269	1.970	2.804	131.4	125.9	123.8	0.0
6ct	1.378[a]	1.436[a]	1.261	1.948	2.781	131.0	124.9[a]	123.8[a]	−2.0[a]
	1.362[b]	1.458[b]					131.0[b]	116.3[b]	159.9[b]
6tt	1.368	1.457	1.251				129.4	117.0	146.3
2cc	1.438	1.476	1.248	1.991	2.829	131.7	122.0	126.9	0.9
2ct	1.438[a]	1.476[a]	1.238	1.984	2.828	132.2	121.9[a]	127.4[a]	1.4[a]
	1.455[b]	1.503[b]					120.8[b]	122.0[b]	120.9[b]
7c	1.385	1.419	1.250	1.957	2.797	131.7	125.0	125.9	0.0
7t	1.373	1.438	1.239				131.2	118.2	177.3
8c	1.362	1.435	1.361[c]				129.6	129.7	14.9
8t	1.358	1.439	1.361[c]				130.8	118.5	−170.9
9c	1.384	1.425	1.232	1.967	2.793	130.5	123.6	126.7	0.0
9t	1.374	1.430	1.226	2.032	2.825	127.9	130.4	122.8	180.0
10c	1.384	1.409	1.218	2.045	2.862	130.0	123.5	131.4	0.0
10t	1.382	1.415	1.206	1.980[d]	2.769[e]	127.4[f]	129.8	127.0	180.0
11c	1.391	1.403	1.247	1.975	2.813	131.6	123.8	129.0	0.0
11t	1.387	1.421	1.236				131.8	121.7	175.4

[a] Cisoid half. [b] Transoid half. [c] *d*(C=C). [d] *d*(F···H). [e] *d*(F···C). [f] Angle (C−H···F).

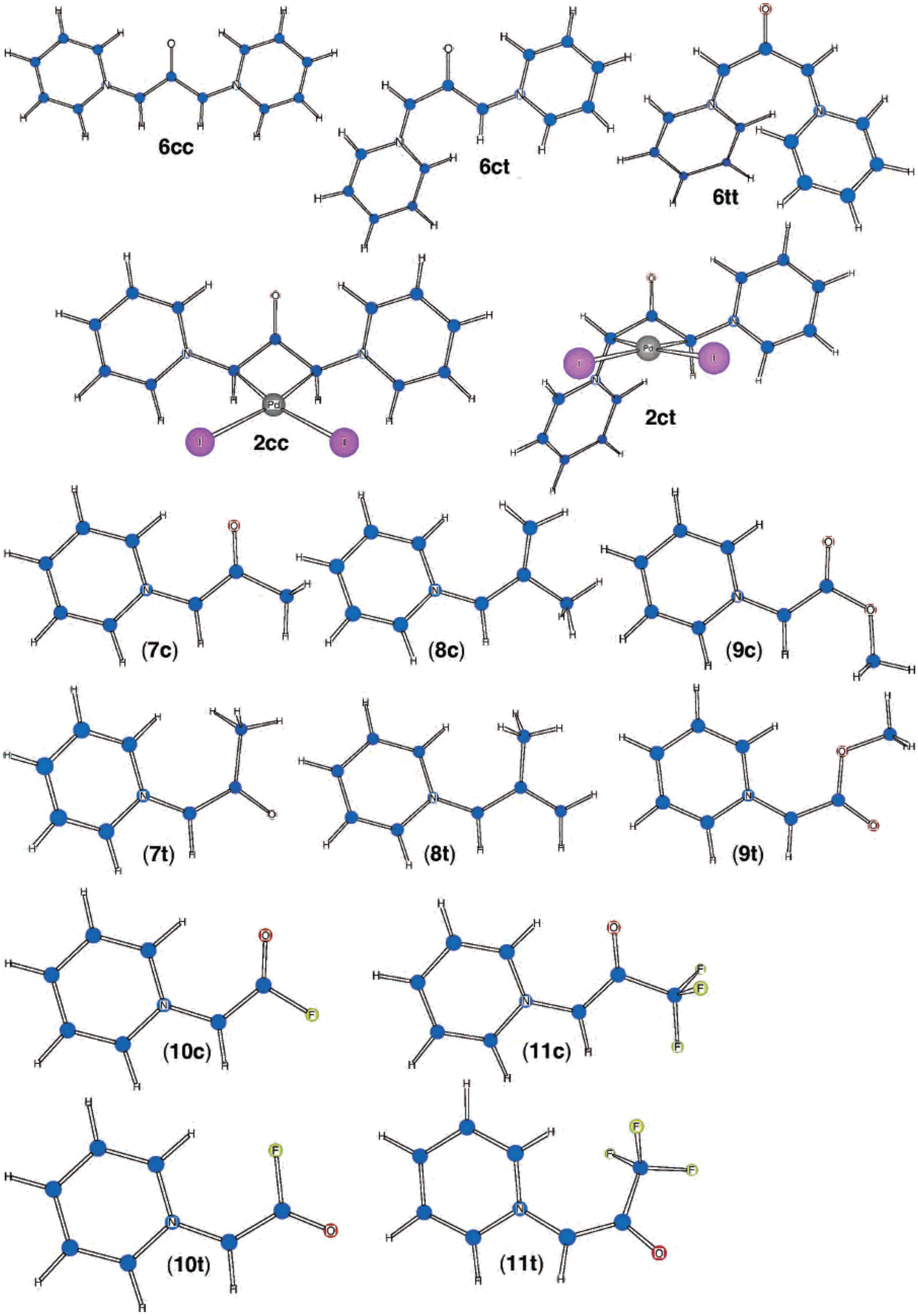
The IR spectra of complexes **3a,c,d** show typical absorptions due to the chelating bis-ylide (about 1600 cm^{-1}) and the O,O′-bonded acac ligands (about 1570 and 1510 cm^{-1}). The NMR spectra of **3a** and **3d** show similar features to those described for **2a** and **2d**, that is, the equivalence of the two halves of the molecule with respect to a symmetry plane containing the C=O group the Pd atom and, in this case, the CH group of the acac ligand. This fact implies that the bis-ylide ligand has not changed its conformation (meso form) on going from **2** to **3**. In the case of complex **3c**, the ^{1}H NMR spectrum shows six different signals in the aromatic region and two well-separated resonances corresponding to the two ylidic C$_\alpha$−H protons, in addition to the expected peaks attributed to the methyl groups of the acac and 2,3-lutidine moieties. Full assignment of all resonances and also of the stereochemistry of **3c** was achieved using selective NOESY-1D and ROESY-1D experiments. The selective saturation of the signal at 5.68 ppm (assigned to the ylidic proton of the lutidine fragment) induces a clear NOE effect on the signal at 5.79 ppm (because of the ylidic proton of the pyridine fragment) and also on the signal at 2.82 ppm (assigned to the 2-Me group of the lutidine). The NOE effect between the two ylidic CH protons is only possible if both protons are located on the same side of the molecular plane, that is, if the bis-ylide adopts the meso form, as observed in **3a** and **3d**. In addition, the observation of an NOE effect between this ylidic C$_\alpha$H proton and the 2-Me group (but not with the H$_6$ proton of the lutidine) implies a restricted rotation of the lutidine around the N−C$_\alpha$ bond (on the NMR time scale) in such a way that the 2-Me group lies in one side of the molecular plane, pointing to the C$_\alpha$H unit, whereas the H$_6$ proton lies on the other side of the molecular plane and points to the carbonyl oxygen. In fact, the signal due to the H$_6$ proton appears in **2c** (9.51 ppm) and **3c** (9.45 ppm) shifted to low field when compared to its position in **1c** (8.95 ppm), probably accounting for this interaction. These shifts are also observed in the H$_{ortho}$ protons of the pyridine ring, but they are clearly smaller (9.16 ppm (**1c**); 9.23 ppm (**2c**), 9.25 ppm (**3c**)). As expected, the selective saturation of the signal due to H$_6$ (9.45 ppm) only produces an NOE effect on the signal assigned to H$_5$ (7.64 ppm). However, the selective saturation of the signal at 5.79 ppm induces clear NOE effects in the signal at 5.68 ppm and in the signal at 9.25 ppm (assigned to the two H$_{ortho}$ protons of the pyridine). The chemical equivalence of the two H$_{ortho}$ protons, as well as the two H$_{meta}$ protons, of the pyridine shows that this fragment is able to rotate around the N−C$_{ipso}$ bond. The measurement of the ^{1}H NMR spectra of complexes **3a** and **3c** at low temperature (CD$_2$Cl$_2$, 183 K) did not result in the splitting of the signals due to the H$_{ortho}$ or H$_{meta}$ protons.

In summary, the synthesis of Pd^{II} complexes with N-bis-ylides, symmetric or asymmetric, derived from pyridine, lutidine, or isoquinoline shows that the bis-ylides bond to the Pd^{II} center as C,C-chelates, forming four-membered metallacycles, and that only one diastereoisomer (the meso form) is obtained.

2. The Bis-Ylide [H$_5$C$_5$N−C(H)C(O)C(H)−NC$_5$H$_5$]. Theoretical Results. At first glance, the behavior of the bis-ylides [Ph$_3$P=C(H)C(O)C(H)=PPh$_3$] and [H$_y$C$_x$N−C(H)C(O)C(H)−NC$_x$H$_y$] seems to be quite similar. Our studies in the conformational preferences of the bis-ylide [H$_3$P=C(H)C(O)C(H)=PH$_3$] and other keto-stabilized P-ylides[1,2] have allowed us to determine that the 1,4-P···O intramolecular interactions are the source of these preferences. Aiming to determine which type of contacts are present in the bis-ylide [H$_5$C$_5$N−C(H)C(O)C(H)−NC$_5$H$_5$] (**6**), we have performed a theoretical DFT study (at the B3LYP level)[11] on the bis-ylide **6** and on the two possible diastereoisomers resulting after Pd-bonding **2cc** and **2ct** (Chart 1, Table 2).

The bis-ylide **6** has been calculated in three extreme conformations: cisoid−cisoid, **6cc**; cisoid−transoid, **6ct**; and transoid−transoid, **6tt**. All have been characterized as minima by analytically computing of the Hessian matrix. The most stable structure is the cisoid−cisoid, **6cc**, having the differences of energy ΔE[(**6ct**) − (**6cc**)] = 42.88 kJ mol^{-1} and ΔE[(**6tt**) − (**6cc**)] = 77.52 kJ mol^{-1}. These values are somewhat similar to those obtained for the bis-ylide [H$_3$P=C(H)C(=O)C(H)=PH$_3$] (34.7 and 88.7 kJ mol^{-1}, respectively).

Chart 1



Several structural changes are observed in the transition **6cc** → **6ct** → **6tt**. The structure of **6cc** is planar (all dihedral angles are 0° or 180°) and symmetrical with respect to the O═C$_{\beta}$ axis, and although the structure of **6ct** shows two well-differentiated halves with respect to the C$_{\beta}$═O axis, the cisoid half is almost planar with small values of the dihedral angles NC$_{\alpha}$C$_{\beta}$O (−2.0°) and C$_{\text{ortho}}$NC$_{\alpha}$C$_{\beta}$ (−5.8° and 174.6°) whereas the transoid half deviates notably from planarity

($NC_\alpha C_\beta O = 159.9°$; $C_{ortho}NC_\alpha C_\beta = -13.0°$ and 169.7°). Conformation **6tt** shows C_2 symmetry with respect to the $C_\beta{=}O$ axis and a complete loss of planarity, defined by the dihedral angles $NC_\alpha C_\beta O$ (146.3°) and $NC_\alpha C_{\alpha'}N'$(52.8°).

The planarity shown by the most stable isomer **6cc** prompted us to investigate if any possible hydrogen bond could be established in this molecule, because we have shown in the Introduction that planar ylides possess,[8] in addition to long N···O distances, the optimal geometric arrangement to the establishment of hydrogen bonds. The O···H distance in **6cc** between the carbonyl oxygen and one of the ortho protons of the pyridinic ring is 1.970 Å, the $O{\cdots}C_{ortho}$ distance is 2.804 Å, and the angle C−H···O is 131.4°. These parameters match very well with the presence of a moderate hydrogen bond[10a] with bond energies in the range 16.7−62.7 kJ mol^{-1}. The obtained value of the energy difference ΔE[(**6ct**) − (**6cc**)] = 42.88 kJ mol^{-1} also matches in this range, taking into account that this value should be due, at least, to the partial loss of resonance and to the cleavage of one hydrogen bond. It is worthy of note that the N···O distance in **6cc** is 2.948 Å, close to the sum of the van der Waals radii (3.02 Å). Thus, the presence of hydrogen bonds, rather than the establishment of N···O contacts, seems to be operating in bis-ylide **6cc**, stabilizing the cisoid−cisoid conformation. The bis-ylide **6ct** also shows the presence of an intramolecular hydrogen bond in the cisoid half of the molecule, characterized by the distances O···H (1.948 Å) and O···C (2.781 Å) and by the angle C−H···O (131.0°).

The C,C-bonding of the bis-ylides **6cc** and **6ct** to the PdI_2 unit gives complexes **2cc** and **2ct** (Chart 1, Table 2). Both complexes were characterized as minima by analytical computation of the Hessian matrix. As expected, the most stable complex is **2cc**, which is the diastereoisomer obtained experimentally (**2a**). The energy difference between the two diastereoisomers is ΔE[(**2ct**) − (**2cc**)] = 43.40 kJ mol^{-1}, which is very close to the value obtained for the free bis-ylides ΔE[(**6ct**) − (**6cc**)] = 42.88 kJ mol^{-1}. These results suggest that the conformational preferences observed in the free bis-ylide seem to be responsible for the stereochemistry adopted by the bonded ligand.

The structural analysis of the calculated complexes **2cc** and **2ct** shows the expected changes (Table 2), (i) the $N{-}C_\alpha$ and $C_\alpha{-}C_\beta$ bond distances are elongated with respect to their corresponding values in **6cc** and **6ct** and (ii) the $C_\beta{=}O$ bond distance is shorter because of the loss of charge delocalization. More interestingly, the orientation of the pyridine rings with respect to the carbonyl group $C_\beta{=}O$ is produced in such a way that the dihedral angle $NC_\alpha C_\beta O$ shows values as small as 0.9 (**2cc**) or 1.4° (cisoid half, **2ct**). This fact allows, or is a consequence of, the establishment of the hydrogen bond between the ortho proton and the carbonyl oxygen, even in the complexed form and in both complexes **2cc** and **2ct**. The parameters of the hydrogen bonds in **2** are slightly longer than those described for the free bis-ylides [O···H = 1.991 (**2cc**); 1.984 Å (**2ct**)]. All these geometrical data indicate that upon coordination of the bis-ylide the C_α pyramidalizes and the hydrogen bond weakens because of the charge transfer to the metal and loss of charge conjugation. This also might be reflected in the rotational barriers of the pyridine moiety. The computed rotational barrier around the $N{-}C_\alpha$ bond for free bis-ylide **6cc** is 100.7 kJ mol^{-1} whereas in the complex **2cc**, amounts to only 14.1 kJ mol^{-1}. The lowering of the rotational barrier is in agreement with NMR data, which suggests that pyridinic rings are able to rotate around the $N{-}C_\alpha$ bond when steric effects are absent (e.g., complex **3c**). However, the N···O distances in these molecules are 2.995 (**2cc**) and 2.997 Å (**2ct**), being both values very close to the sum of the van der Waals radii. Thus, the possibility of the N···O contacts as a source of discrimination will not be longer considered.

In the discussion of the structure of complexes **2** from the NMR data, we have assumed that the observed symmetry between the two halves of the molecule should be due to a plane of symmetry containing the Pd atom and the CO group (C_s symmetry). We have discarded the structure in which the PdC_3O core is not planar, based on our previous experience with P-ylides[13] and on recent results in very related systems.[14] These facts have been confirmed by calculation of structures **2cc** and **2ct**. We have calculated the energy of the planar structure of **2ct**, imposing C_2 symmetry. The characterization of the C_2-symmetric complex by computation of the Hessian matrix revealed that this is not a true minumum but a transition state. We have observed one imaginary frequency whose associated normal mode corresponds to the inversion of the C═O unit. The energy of this structure lies 38.15 and 81.6 kJ mol^{-1} higher than **2ct** and **2cc**, respectively. Thus, despite the fact that we cannot discard the interconversion between different isomers of **2ct** in solution, it is clear that structure **2cc** remains as the overall minimum and that **2cc** is the most probable isomer.

The comparison of **2cc** with the X-ray structure of *cis*-$PdI_2[\eta^3\text{-}\{CH(MeIm)\}_2CO]$[14] (Table 3) shows that the two molecules are almost isostructural. The correlation of bond distances and angles gives, within experimental error, identical values for the basic skeleton, even if we consider that the groups are different (imidazolium versus pyridinium). This correlation gives proof of the goodness of the structure **2cc** calculated with this methodology.

Because of the intrinsic importance of the subject involved (i.e., conformational preferences due to hydrogen bonds), we have performed a detailed DFT study (B3LYP level)[11] on model pyridinium ylides to unambiguously determine the presence or absence of the hydrogen bonds and their relationship with the observed conformational preferences.

3. Behavior of the N−Ylides $[H_5C_5N{-}C(H)C(O)R]$. The conformational preferences of keto-stabilized pyridinium ylides $[H_5C_5N{-}C(H)C(O)R]$ (R = Me ,**7**; OMe, **9**; F, **10**; CF_3, **11**) have been studied. We have also studied the ylide $[H_5C_5N{-}CH{-}C({=}CH_2){-}Me]$ (**8**), for comparative purposes and the rotational barriers around the $C_\alpha{-}C_\beta$ bond for **7**, **8**, and **9** in which potential energy profiles were built. In all cases, the minima and transition state were characterized by analytical computation of the Hessian matrix. The energy differences between the transoid and cisoid conformations ($\Delta E_1 = E_{trans} - E_{cis}$) and the rotational barriers ($\Delta E_2 =$

Table 3. Structural Comparison of (**2**) and $PdI_2[\eta^3\text{-}\{CH(MeIm)\}_2CO]^a$

parameter	**2cc**	**2ct**	$PdI_2[\eta^3\text{-}\{CH(MeIm)\}_2CO]$
$N-C_\alpha$	1.438	1.438^b	1.448(7)
		1.455^c	1.430(7)
$C_\alpha-C_\beta$	1.476	1.476^b	1.446(8)
		1.503^c	1.458(8)
$C_\beta=O$	1.248	1.238	1.261(7)
Pd−C	2.165	2.178^b	2.085(6)
		2.129^c	2.090(6)
Pd−I	2.687	2.700^b	2.6746(6)
		2.693^c	2.6691(6)
IPdI	99.3	98.0	100.9(2)
$PdC_\alpha C_\beta$	83.0	83.0^b	81.8(3)
		84.2^c	81.4(3)
$C_\alpha PdI$	97.5	97.0^b	96.5(2)
		96.8^c	95.7(2)
$C_\alpha PdC_\alpha$	65.5	68.0	66.8(2)
$PdC_\alpha N$	122.3	122.9^b	122.4(3)
		112.4^c	122.3(4)
$C_\alpha C_\beta C_\alpha$	104.9	108.0	104.7(5)
$C_\alpha C_\beta O$	126.9	127.4^b	127.5(7)
		122.0^c	125.8(5)
$NC_\alpha C_\beta$	122.0	121.9^b	117.8(5)
		120.8^c	118.0(5)
O···H	1.991	1.984	
O···C	2.829	2.828	
C−H···O	131.7	132.2	
N···O	2.995	2.997	

[a] Data from ref 14. [b] Cisoid half. [c] Transoid half.

Table 4. Calculated Values of ΔE_1 ($E_{trans} - E_{cis}$), ΔE_2 ($E_{TS} - E_{cis}$) (kJ mol^{-1}), and NPA Atomic Charges for Ylides **2** and **6**−**11**

compd	ΔE_1	ΔE_2	q(O)	q(N)	$q(C_\alpha)$	$q(H_o)$	$q(H_{o'})$
6cc	0.0		−0.715	−0.281	−0.174	0.282	0.232
6ct	42.88		−0.672	−0.278^a	−0.218^a	0.286	0.233
				−0.287^b	−0.155^b	0.236	0.242
6tt	77.52		−0.618	−0.288	−0.201	0.238	0.248
2cc	0.0		−0.671	−0.287	−0.304	0.285	0.269
2ct	43.40		−0.611	−0.288^a	−0.327^a	0.286^a	0.269^a
				−0.288^b	−0.309^b	0.279^b	0.254^b
7	47.00	107.3	−0.656	−0.275	−0.227	0.286	0.238 (**7c**)
			−0.598	−0.281	−0.200	0.241	0.241 (**7t**)
8	9.01	29.06	−0.078^c	−0.282	−0.123	0.241	0.232 (**8c**)
			−0.044^c	−0.287	−0.095	0.231	0.230 (**8t**)
9	−9.19	83.27	−0.655	−0.271	−.287	0.285	0.236 (**9c**)
			−0.636	−0.275	−0.242	0.266	0.239 (**9t**)
10	18.06		−0.636	−0.274	−0.292	0.280	0.241 (**10c**)
			−0.585	−0.275	−0.287	0.265	0.242 (**10t**)
11	48.69		−0.629	−0.276	−0.231	0.287	0.244 (**11c**)
			−0.574	−0.281	−0.232	0.253	0.246 (**11t**)

[a] Cisoid. [b] Transoid. [c] $q(CH_2)$.

$E_{TS} - E_{cis}$) are collected in Table 4. The optimized cisoid and transoid structures for **7**−**11** are presented in Chart 1.

The ylide $[H_5C_5N-C(H)C(O)Me]$ **(7)** shows a value of ΔE_1 of 47.00 kJ mol^{-1}, being the most stable cisoid structure **7c** (see Computational Details). This value is very similar to that obtained for ylide **6ct** (42.88 kJ mol^{-1}) and implies a strong preference for the cisoid conformation of the ylide. The cisoid preference can also be inferred from the comparison of the experimental IR data for pyridinium ylides (1500−1530 cm^{-1})[15a,d] with those calculated for the structures **7c** (1655 cm^{-1}), **7TS** (1785 cm^{-1}), and **7t** (1674 cm^{-1}). The unique ylide containing a single keto-stabilizing substituent characterized structurally by X-ray diffraction methods[8c] shows the cisoid conformation. However, the value of ΔE_1 for the allyl semistabilized ylide **8** is only 9.01 kJ mol^{-1}, this meaning that the two conformations **8c** and **8t** are almost isoenergetic. The value of the energy barrier ΔE_2 for **8** is 29.06 kJ mol^{-1} and can be mainly attributed to the loss of stabilization by resonance in the transition state.

The structures of **7c** and **7t** show some noteworthy facts. First, compound **7c** is rigorously planar, whereas **7t** shows slight deviations from planarity (Table 2). In both derivatives, the bond distances and angles are found in the usual ranges for these types of bonds, but the comparison of **7c** and **7t** shows a more polarized skeleton $NC_\alpha C_\beta O$ in **7c**. Moreover, during the rotational process **7c** → **7TS** → **7t**, as the dihedral angle $NC_\alpha C_\beta O$ increases (and also the energy increases), the $N-C_\alpha$ and $C_\beta-O$ distances decrease while the $C_\alpha-C_\beta$ bond distance increases until the TS is reached ($NC_\alpha C_\beta O = 89.4°$). This implies that the TS is the less polarized structure. After the TS, the opposite behavior is observed because of a new stabilization by resonance. Finally, the distance in **7c** between the cisoid ortho H atom of the pyridine ring and the carbonyl oxygen is 1.957 Å (shorter even than in **6cc**), and the corresponding O···C distance and C−H···O angle values are 2.797 Å and 131.7°, strongly suggesting a C−H···O hydrogen bond.

The stabilization provided by this hydrogen bond in the cisoid form should also be reflected in the rotational barrier of the pyridine around the $N-C_\alpha$ bond in structure **7c**. The calculated value in gas phase is 86.5 kJ mol^{-1}, only slightly smaller than that calculated for bis-ylide **6cc**. The ^1H NMR spectrum of **7**, prepared as reported previously[15] in dry CD_2Cl_2 at room temperature, shows a single signal for both H_{ortho} protons, showing the free rotation of the NC_5H_5 moiety around the $N-C_\alpha$ bond. After being cooled, this signal broadens and the coalescence temperature T_c is attained at 183 K. The narrow limit could not be reached by further cooling. It may seem that our computed value does not account for experimental observations. However, the high polarization of the TS structure describing the pyridine rotation suggests that the solvent could play a key role in its stabilization. In fact, simulation of CH_2Cl_2 by means of Tomasi polarized continuum model (PCM) reaction-field calculations shows that solvent effects significantly lower the energy barrier to 62.0 kJ mol^{-1}. Moreover, we have not observed any significant change in the relative energies of cisoid and transoid isomers upon introduction of diffuse functions in our calculation (basis set BII, see Computational Details). However, in the case of the rotation barrier for free ylide **7c**, in which a highly polarized TS structure is involved, diffuse functions were revealed to be important. Thus, recalculation of solvent effects with basis set BII further reduces the rotation barrier from 62 to 41 kJ mol^{-1}, the latter value being in better agreement with experimental results.

The results obtained with ylide $[H_5C_5N-C(H)C(O)CF_3]$ **(11)** (Tables 2 and 4; Chart 1) are quite similar to those described for **7**. However, the ester-stabilized ylide $[H_5C_5N-C(H)C(O)OMe]$ (**9**) shows a different behavior. In this case the value of ΔE_1 is small (−9.19 kJ mol^{-1}) and favors slightly the transoid conformation. The value of the rotational barrier in **9**, however, is high ($\Delta E_2 = 83.27$ kJ mol^{-1}). A sensible explanation for the energetic equilibration of the two isomers, but also showing a high value of ΔE_2, could be obtained by taking into account that ylide **9** has one oxygen atom in both sides of the ylidic carbon C_α and that the pyridinium ring is able to establish hydrogen bonds with the two oxygens, resulting in a small difference of energy between the two rotational isomers. However, the high value of ΔE_2 can be interpreted, as for **7**, as the result of sum of the loss of resonance, the loss of the hydrogen bond, and the hindered rotation around the $C_\alpha-C_\beta$ bond at the transition state.

The results obtained for the ylide $[H_5C_5N-C(H)C(O)F]$ **(10)** are similar to those of **9**, because the presence of the very electronegative F atom as a substituent at the carbonyl group results in two conformations with a small difference of energy (18.06 kJ mol^{-1}). This is due to the establishment of an hydrogen bond C−H···O in the cisoid conformation **10c** and another hydrogen bond C−H···F in the transoid conformation **10t**, characterized by the following parameters: F···H = 1.980 Å, F···C = 2.769 Å, and C−H···F = 127.4°. Thus, the presence of electronegative atoms seems to be necessary in order to discriminate between the two conformations in such a way that if one strongly electronegative substituent is attached to the C_β atom, then the formation of hydrogen bonds with one ortho proton of the pyridinium ring favors the cisoid conformation, whereas if two electronegative atroms are bonded to the C_β atom, then two hydrogen bonds can be established, one in each conformation, and these become almost isoenergetic.

4. Bader Analysis of Intramolecular Interactions. Bader analysis of electron density has been largely applied in the literature to the study and characterization of weak interactions and also to the study of hydrogen bond interactions.[10] We have applied the Bader's atoms in molecules (AIM) theory[16] to the study of the different conformational isomers of N-ylides **7**, **9**, and **10**, as representative examples of 1,6-C−H···X (X = O, F) intramolecular interactions in planar pyridinium ylides. For structures **7c**, **9c**, **9t,** and **10c**, the existence of an intramolecular C−H···O interaction was confirmed by the topological analysis of the electron density and for compound **10t** the existence of an intramolecular C−H···F interaction. These interactions were characterized by the corresponding bond critical points (bcp's) in the electronic charge density $\rho(r)$. Also, ring critical points (rcp's) were localized between the atoms X (X = O, F), C_β, C_α, N, C_{ortho}, and H_{ortho}, further proving the existence of C−H···O and C−H···F interactions.

In addition, AIM theory provides a set of practical tools to gauge the variation in charge density and bonding nature which occur upon structural changes. Recently, Koch and Popelier have proposed a set of criteria based on AIM theory to characterize hydrogen bonds.[17] These criteria have been then conveniently summarized by Pacios and Gómez.[18] Here, we have considered a subset of four criteria that comprises the local topological properties of $\rho(r)$. Similar analyses have been very recently reported on the study of intramolecular hydrogen bond interactions.[19,20] The first criterion states that a bond critical point should be found between the donor hydrogen and the acceptor atoms, and the topology of the bond path should ensure that the path links the two atoms. Second, the electron density $\rho(r)$ at the bcp should be about 1 order of magnitude smaller than those for a covalent bond, typically ranging between 0.002 and 0.04 au. Third, the Laplacian of the charge density $\nabla^2\rho(r)$ at the bcp should be positive, typically ranging between 0.015 and 0.15 au.[21] Fourth, a mutual interpenetration of hydrogen and acceptor atoms should be observed. This criterion compares the nonbonding radius of hydrogen (r^0_H) and acceptor (r^0_A) atoms, with their corresponding bonding radii (r_H and r_A). The nonbonding radius (r^0) is taken as the equivalent to the van der Waals radius, whereas the bonding radius (r) is defined as the distance between the nucleus and the corresponding bcp. Thus, Koch and Popelier propose not only that a positive mutual penetration ($\Delta r_H + \Delta r_A > 0$) is necessary but also that the hydrogen atom should be more penetrated than the acceptor atom ($\Delta r_H > \Delta r_A$).

Table 5. Topological Properties at the Bond Critical Points of C−H···X (X = O, F) Intramolecular Interactions of the Ylides Structures **7**, **9**, and **10**; and MDAE[a]

structure	$\rho(r)^b$	$\nabla^2\rho(r)^b$	$\Delta r_H{}^c$	$\Delta r_A{}^c$	$\Delta r_H + \Delta r_A{}^c$	$\Delta_{geo+el+lap}{}^d$
7c	0.030	0.099	0.463	0.298	0.761	0.106
9c	0.025	0.083	0.453	0.297	0.750	0.112
9t	0.025	0.094	0.404	0.283	0.687	0.084
10c	0.029	0.099	0.410	0.262	0.672	0.091
10t	0.024	0.086	0.414	0.271	0.685	
MDAE[a]	0.014	0.048	0.248	0.137	0.385	0.062

[a] 1-Methoxy-2-(dimethylamino)ethane, MDAE (ref 22). [b] Electron charge density, $\rho(r)$, Laplacian, $\nabla^2\rho(r)$, in au. [c] Penetration of the hydrogen atom, Δr_H, penetration of the acceptor atom Δr_A, mutal penetration $\Delta r_H + \Delta r_A$, in Å. [d] Modified Grabowski's complex parameter $\Delta_{geo+el+lap}$, (ref 25).

The results of this analysis are summarized in Table 5. It is clear from these data that the values of $\rho(r)$, $\nabla^2\rho(r)$, and mutual interpenetration fully fulfill the Koch and Popelier's criteria (see the first five columns of results in Table 5). Moreover, we have performed an analogous analysis for the experimentally characterized 1,6-C−H···O hydrogen bond interaction in 1-methoxy-2-(dimethylamino)ethane (MDAE).[22] The results for the computed most stable isomer[22] are also in agreement with the above criteria (Table 5). Therefore, the 1,6-C−H···O interactions characterized for planar N-ylides can be unambiguously assigned to true hydrogen bonds. It is worthy of note that this interaction was suspected 30 years ago[23a] and, moreover, that the cisoid conformation of the N-ylide **7c** has recently been studied by means of theoretical calculations.[23b] There, the authors have clearly

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(21) One of the advantages of using the AIM method is that the results are system independent and not highly basis set dependent (see ref 16).

(22) Matsura, H.; Yoshida, H.; Hieda, M.; Yamanaka, S.; Harada, T.; Shin-Ya, K.; Ohno, K. *J. Am. Chem. Soc.* **2003**, *125*, 13910.

(23) (a) Phillips, W. G.; Ratts, K. W. *J. Org. Chem.* **1970**, *35*, 3144. (b) Dega-Szafran, Z.; Schroeder, G.; Szafran, M.; Szwajka, A.; Leska, B.; Lewandowska, M. *J. Mol. Struct.* **2000**, *555*, 31.

noticed the presence of a contact between the ortho proton of the pyridinium ring and the carbonyl oxygen, but they have discarded the possibility of a hydrogen bond between these two groups exclusively on the basis of the small value of the angle C−H···O without any other verification.[23b] At our computed level, the angle C−H···O for **7c** is 131.7°, still larger than that for the most stable MDAE isomer, 123.2°.

It has been shown that $\rho(r)$ at the bcp is related to the bond strength; thus the larger the value $\rho(r)$ at the bcp, the stronger the bond.[16,24] Inspection of data in Table 5 reveals that C−H···O interactions in the ylides show larger values of $\rho(r)$ as compared to that of MDAE, indicating stronger hydrogen bond interaction for planar N-ylides than for MDAE. In fact, for MDAE, the energy difference between the most and the least stable conformers was computed to be about 4 kJ mol^{-1},[22] whereas the energy difference between **7c** (C−H···O interaction) and **7t** (no C−H···O interaction) is 47.0 kJ mol^{-1}. (The values of $\rho(r)$ at the bcp's also reflect the stronger hydrogen bond interactions at the free bis-ylides as compared to the complexes. Thus, the values of $\rho(r)$ for **6cc** and **6ct** (0.030 and 0.031 au, respectively) are slightly larger than those for **2cc** and **2ct** (0.028 and 0.028 au, respectively).) The precise measure of intramolecular bond strength is not an easy task; one could always argue that its estimation as the difference in energy between interacting and noninteracting conformers is not correctly accounting for intramolecular bond strength, because other factors such as strain effects and electronic steric repulsions are embedded in these energy differences. Here, we explore an alternative procedure based on AIM properties for estimating intramolecular bond strength.

Grabowski has proposed a complex parameter ($\Delta_{\text{geo+el+lap}}$) based on structural data and topological parameters for describing hydrogen bond strength.[25] The results of his work showed linear correlations between $\Delta_{\text{geo+el+lap}}$ and hydrogen bond energies for a number of different intermolecular hydrogen bond interactions. The modified Grabowski's complex parameter $\Delta_{\text{geo+el+lap}}$ is defined as follows

$$\Delta_{\text{geo+el+lap}} = \{[(r_{\text{C−H}} - r^0_{\text{C−H}})/r^0_{\text{C−H}}]^2 + [(\rho_{\text{C−H}} - \rho^0_{\text{C−H}})/\rho^0_{\text{C−H}}]^2 + [(\nabla^2\rho_{\text{C−H}} - \nabla^2\rho^0_{\text{C−H}})/\nabla^2\rho^0_{\text{C−H}}]^2\}^{1/2}$$

where $r_{\text{C−H}}$, $\rho_{\text{C−H}}$, and $\nabla^2\rho_{\text{C−H}}$ correspond to the donor-hydrogen bond involved in the hydrogen bonding and $r^0_{\text{C−H}}$, $\rho^0_{\text{C−H}}$, and $\nabla^2\rho^0_{\text{C−H}}$ correspond to the donor-hydrogen bond not involved in the hydrogen bonding. Chen and Naidoo[26] have used this complex parameter for evaluating intramolecular hydrogen bond strength through construction of correlation curves from intermolecular interactions between pairs of functional groups.

We define two pairs of intermolecular C−H···O interactions, (i) an acceptor ketonic oxygen [O=C(H)−CH$_3$] interacting with the ortho C−H donor of the nonsubstituted pyridinium ylide [H$_5$C$_5$N−CH$_2$] and (ii) an acceptor enolate oxygen [(−)OC(H)=CH$_2$] interacting with the same C−H donor group of [H$_5$C$_5$N−CH$_2$]. Note that these two pairs of interacting functional groups could represent the two extreme cases of resonance in the ketonic α-substituents of N-ylides. The computed interaction energies for the two pairs are 9.7 and 58.1 kJ mol^{-1}, respectively, whereas the calculated $\Delta_{\text{geo+el+lap}}$ parameters are 0.040 and 0.110, respectively. These two sets of values could be considered the lower (9.7 kJ mol^{-1}, 0.040) and upper (58.1 kJ mol^{-1}, 0.110) limits of the hydrogen bond interaction in keto-stabilized pyridinium ylides. In fact, all the calculated values of the $\Delta_{\text{geo+el+lap}}$ parameter lie between 0.04 and 0.11 for intramolecular C−H···O interactions (see Table 5). In the case of N-ylides, the $\Delta_{\text{geo+el+lap}}$ values are substantially closer to the upper than to the lower limit, suggesting that the intramolecular hydrogen bond interactions reach values near 58 kJ mol^{-1}. However, for MDAE, $\Delta_{\text{geo+el+lap}}$ is much smaller, being closer to the lower limit (9.7 kJ mol^{-1}). These results are fully consistent with the energetic differences found between conformers.[27] Assuming an ideal linear correlation between the interaction energy and the $\Delta_{\text{geo+el+lap}}$ parameter, one may easily determine the interaction energy of intramolecular hydrogen bonds. Obviously, this is a rough approximation, but it is still meaningful for our purposes. Hence, the estimated C−H···O interaction energy for **7c** structure is about 55 kJ mol^{-1}, qualitatively very similar to the energy preference (47.0 kJ mol^{-1}) of cisoid **7c** with respect to the transoid **7t**, in which no hydrogen bond is present. Thus, we can conclude that most of the conformational preference observed in planar keto-stabilized pyridinium ylides comes as a result of the intramolecular hydrogen bond interaction.

The nature of the hydrogen bond interaction also should be reflected in the formal charges, undergoing a detectable change depending whether the hydrogen bond is present or is not. The natural population analysis (NPA) charges of representative atoms are shown in Table 4. The distribution of NPA charges in the pyridinium ring gives negative values (about −0.28) for the N atom (despite the behavior of other ylides, in which the heteroatom supports the positive charge) and for the carbon atoms of the pyridinium unit (close to zero for the ortho carbons and ranging −0.24 to −0.30 for the meta and para carbons), whereas the positive charge is concentrated in the H atoms (typically 0.23), forming a positive belt around a negative core. These facts are well established in the literature.[28] However, as expected, the charges of the ortho protons are different depending if they are involved or not in the hydrogen bond, as it can be clearly seen in Table 4. The NPA charge for H atoms not involved

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(24) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001.

(25) Grabowski, S. J. *J. Phys. Chem. A* **2001**, *105*, 10739.

(26) Chen, J. Y. J.; Naidoo, K. J. *J. Phys. Chem. B* **2003**, *107*, 9558.

(27) Grabowski has shown that the correlations improve when the sample consists only of hydrogen bonds with the same proton donor and the same type of proton acceptor (ref 25). Thus, we expect a worse correlation for the intramolecular C−H···O interactions involving the oxygen of an ester than that with the oxygen of a ketonic group.

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in a H bond is around 0.23, whereas that of the H atoms belonging to the hydrogen bond increases up to 0.28.

Although C−H···O hydrogen bonds are usually classified as weak interactions, all of the above results indicate that for planar α-stabilized ylides the interaction is about 1 order of magnitude higher than that found for typical weak hydrogen bonds (<16.7 kJ mol^{-1}),[10] as seem to be the case for MDAE. Two factors are at work enhancing the C−H···O interaction, the charge assistance[10l,m] and the so-called π-bond cooperativity or resonance assisted hydrogen bonding.[10,29] It is known that the acidity and therefore the donor strength of A−H are dramatically enhanced by a positive charge A$^+$−H. Indeed, an exceptionally high bond energy of 38.9 kJ mol^{-1} was calculated for $H_3N^+{-}CH_3 \cdots OH_2$.[10l,m] In the pyridinium ylides most of the positive charge carried by the ring is spread out by the hydrogen atoms, increasing its acidity and consequently their electrostatic interaction with the acceptor atoms. Moreover, the donor and acceptor pairs of α-stabilized ylides are connected by the resonant π system of the ylide skeleton. The electronic charge then can flow through the π bonds polarizing the C−H and O groups and, consequently, enhancing the hydrogen bond interaction. None of the two factors is present in the closely related MDAE compound. C−H···O bonds stronger than 16.7 kJ mol^{-1} were predicted to occur when very acidic C−H or very basic acceptor groups are involved.[10a] Our study confirms this prediction and gives evidence on the existence of C−H···O interactions that can be classified as moderate,[10l,m] enlarging considerably the energy range spanned by such interactions.

Conclusions

The reaction of Pd(OAc)$_2$ with bis-pyridinium salts **1a,c,d** gives the N-bis-ylide complexes *cis*-[PdX$_2${η^2-[CH(NC$_x$H$_y$)]$_2$-C(O)}] **(2a,c,d)**, which further react with AgClO$_4$ and Tl(acac) to give [Pd(acac-O,O′){η^2-[C(H)NC$_x$H$_y$]$_2$CO}]ClO$_4$ **(3a,c,d)**. Complexes **2** and **3** have been obtained as single diastereoisomers (meso form, RS/SR configurations at the C$_\alpha$ atoms) due to the presence of strong conformational preferences in the free bis-ylides. The bis-ylide **6** and the ylides [H$_5$C$_5$N−C(H)C(O)R] (R = Me, **7**; OMe, **9**; F, **10**; CF$_3$, **11**) have been studied through DFT calculations at the B3LYP level, showing that the planar and cisoid arrangements are the most stable structures when only one electronegative atom is present at the C$_\alpha$-substituent, whereas cisoid−transoid equilibration occurs if two electronegative atoms are present. This study also suggests the presence of intramolecular 1,6-C−H···O hydrogen bonds between the ortho-proton of the pyridine ring and the carbonyl oxygen. The topological analysis of the electron density proved the existence of intramolecular (N)C−H···A (A = O, F) contacts, which were confirmed as true hydrogen bonds by the corresponding values of $\rho(r)$, $\nabla^2\rho(r)$, and mutual interpenetration. Moreover, on the basis of AIM theory and previous works, we propose a procedure to estimate the bond strength of intramolecular hydrogen bond interactions. The results indicate that the intramolecular hydrogen bond is responsible for most of the conformational preferences observed in planar α-stabilized N-ylides, which are transferred to the PdX$_2$ fragment giving a single diastereoisomer. The comparison with the closely related 1,6-(N)C−H···O intramolecular hydrogen bond interaction in the experimentally characterized MDAE compound reveals that, in the case of planar N-ylides, the interaction is about 1 order of magnitude stronger. This is probably due to the charge assistance and to the π-bond cooperativity effect induced by the π system of the ylide skeleton. Thus, these interactions should be classified as moderate hydrogen bonds. Upon coordination, the hydrogen-bond interaction of pyridinium ylides weakens, as reflected in the lowering of computed rotation barriers and NMR data. Nevertheless, the experimentally observed diastereoisomeric specificity of the complexes is predetermined by the conformational preferences of the free pyridinium ylides, in which the hydrogen bonds play a key role.

Experimental Section

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution. (*J. Chem. Educ.* **1973**, *50*, A335−A337.)

General Methods. Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyzer. Infrared spectra (4000−200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra (δ in ppm, J in Hz) were recorded in CD$_2$Cl$_2$ or DMSO-d_6 solutions at room temperature (other temperatures were specified) on Bruker Avance-400 or ARX-300 spectrometers, operating at 400.13 and 300.13 MHz, respectively; ^{1}H and ^{13}C{^{1}H} NMR were referenced using the residual solvent signal as internal standard, whereas ^{31}P{^{1}H} NMR spectra were externally referenced to H$_3$PO$_4$ (85%).

Synthesis of 1a. Compound **1a** was prepared following the previously described procedure.[12] A solution of 0.723 mL of acetone (9.84 mmol) and 5.00 g of I$_2$ (19.70 mmol) in 25 mL of dry pyridine was refluxed for 4 h and then stirred overnight at room temperature. The resulting solid **1a** was filtered, washed with water (10 mL), THF (20 mL), and Et$_2$O (50 mL), and dried in vacuo. Obtained: 4.24 g (92.0% yield).

Anal. Calcd for C$_{13}$H$_{14}$I$_2$N$_2$O: C, 33.36; H, 3.01; N, 5.98. Found: C, 33.51; H, 3.05; N, 6.02. IR (ν, cm^{-1}): 1747 (ν_{CO}). ^{1}H NMR (DMSO-d_6, δ): 6.07 (s, 4H, NCH$_2$), 8.28 (pseudot, 4H, H$_m$, py, $^3J_{HH}$ = 6.6), 8.74 (t, 2H, H$_p$, py, $^3J_{HH}$ = 7.8), 8.90 (d, 4H, H$_o$, py, $^3J_{HH}$ = 5.4). ^{13}C{^{1}H} NMR (DMSO-d_6, δ): 69.79 (NCH$_2$), 131.61 (C$_m$, py), 149.80 (C$_o$, py), 150.73 (C$_p$, py), 197.22 (CO).

Synthesis of 2a. To a suspension of **1a** (0.417 g, 0.89 mmol) in CH$_2$Cl$_2$ (25 mL), Pd(OAc)$_2$ (0.200 g, 0.89 mmol) was added. The resulting suspension was refluxed for 4 h. During the reaction time, the color of the suspended solid gradually changes from orange to brown. After being cooled to room temperature, the precipitated solid was filtered, washed with additional CH$_2$Cl$_2$ (25 mL) and Et$_2$O (25 mL), air-dried, and identified as **2a**. Obtained: 0.506 g (99.3% yield).

Anal. Calcd for C$_{13}$H$_{12}$I$_2$N$_2$OPd: C, 27.27; H, 2.11; N, 4.89. Found: C, 27.01; H, 1.96; N, 4.93. IR (ν, cm^{-1}): 1595 (ν_{CO}, ylide). ^{1}H NMR (DMSO-d_6, δ): 5.84 (s, 2H, PdC(H)N), 8.08 (pseudot,

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[29] Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023.

4H, H_m, py, $^3J_{HH} = 6.8$), 8.48 (t, 2H, H_p, py, $^3J_{HH} = 7.2$), 9.26 (d, 4H, H_o, py, $^3J_{HH} = 6.0$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 74.90 (PdC(H)N), 127.72 (C_m, py), 144.55 (C_p, py), 144.91 (C_o, py). (The signal due to the CO group was not observed.)

Synthesis of 3a. To a suspension of **2a** (0.200 g, 0.349 mmol) in 50 mL of a mixture CH_2Cl_2/acetone (9/1), $AgClO_4$ (0.072 g, 0.349 mmol) was added. The resulting suspension was stirred at room temperature with exclusion of light for 30 min, and then Tl(acac) (0.106 g, 0.349 mmol) was added and stirred for additional 30 min. The gray suspension was filtered over Celite, and the resulting yellow solution was evaporated to dryness. Treatment of the oily residue with Et_2O (20 mL) and continuous stirring gives **3a** as a yellow solid, which was filtered, washed with Et_2O (20 mL), and dried in vacuo. Obtained: 0.120 g (66.4% yield).

Anal. Calcd for $C_{18}H_{19}ClN_2O_7Pd$: C, 41.80; H, 3.70; N, 5.42. Found: C, 41.64; H, 3.63; N, 5.33. IR (ν, cm^{-1}): 1601 (ν_{CO}, ylide), 1573, 1521 (ν_{CO}, acac). ^1H NMR (CD_2Cl_2, δ): 1.93 (s, 6H, Me, acac), 5.41 (s, 1H, CH, acac), 5.65 (s, 2H, Pd−C(H)N), 7.96 (pseudot, 4H, H_m, py, $^3J_{HH} = 7.0$), 8.43 (t, 2H, H_p, py, $^3J_{HH} = 7.6$), 9.28 (d, 4H, H_o, py, $^3J_{HH} = 6.8$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 27.96 (Me, acac), 66.69 (Pd−C(H)N), 100.52 (CH, acac), 127.86 (C_m, py), 144.95 (C_o, py), 145.01 (C_p, py), 168.63 (CO, ylide), 187.06 (CO, acac).

Synthesis of 4a. To a stirred solution of **3a** (0.154 g, 0.297 mmol) in MeOH (25 mL) at room temperature, HCl (0.6 mL of a 0.5 M solution of HCl in MeOH, 0.30 mmol) was added. The precipitation of a yellow solid **4a** was immediate. The resulting suspension was filtered, and the yellow solid of **4a** was washed with MeOH (5 mL) and Et_2O (25 mL) and dried in vacuo. Obtained: 0.125 g (92.6% yield).

Anal. Calcd for $C_{26}H_{24}Cl_4N_4O_{10}Pd_2$: C, 34.42; H, 2.66; N, 6.18. Found: C, 34.08; H, 2.74; N, 6.25. IR (ν, cm^{-1}): 1588, 1567 (ν_{CO}, ylide). ^1H NMR (DMSO-d_6, δ): 6.04 (s, 1H, Pd−C(H)N), 8.10 (s, broad, 2H, H_m, py), 8.55 (t, 1H, H_p, py, $^3J_{HH} = 7.6$), 9.30 (d, 2H, H_o, py, $^3J_{HH} = 6.8$).

Synthesis of 5a. To a suspension of **4a** (0.050 g, 0.055 mmol) in CH_2Cl_2 (25 mL), PPh_2Me (20.5 μL, 0.11 mmol) was added. The initial yellow suspension gradually dissolved, and after 30 min stirring at room temperature a yellow solution was obtained. This solution was evaporated to dryness, and the oily residue was treated with Et_2O (20 mL), giving **5a** as a lemon-yellow solid which was filtered, washed with additional Et_2O (2 × 10 mL), and dried in vacuo. Obtained: 0.044 g (61% yield).

Anal. Calcd for $C_{26}H_{25}Cl_2N_2O_5PPd$: C, 47.76; H, 3.85; N, 4.28. Found: C, 47.85; H, 3.79; N, 4.01. IR (ν, cm^{-1}): 1595 (ν_{CO}, ylide). ^1H NMR (CD_2Cl_2, δ): 2.06 (d, 3H, PMe, $^2J_{PH} = 9.6$), 5.87 (s, 1H, Pd−C(H)N cis P), 6.02 (d, 1H, Pd−C(H)N trans P, $^3J_{PH} = 11.2$), 7.27−7.57 (m, 12H, PPh_2 + $2H_m$(py)), 7.92 (pseudot, 2H, H_m, py, $^3J_{HH} = 7.2$), 8.06 (t, 1H, H_p, py, $^3J_{HH} = 7.6$), 8.26 (t, 1H, H_p, py, $^3J_{HH} = 7.6$), 8.57 (d, 2H, H_o, py, $^3J_{HH} = 6.8$), 9.33 (d, 2H, H_o, py, $^3J_{HH} = 6.8$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 12.18.

Synthesis of 1b. To a solution of 2,3-lutidine (1.84 mL, 16.21 mmol) in 25 mL of freshly distilled toluene under Ar atmosphere, 1,3-dibromoacetone (0.500 g, 1.621 mmol) was added. The initial yellow solution changed gradually its appearance, and after 30 min stirring at room temperature, a brown suspension was obtained. This suspension was filtered, and the solid was washed exhaustively with Et_2O to give the pyridinium salt **1b** as an orange solid. Obtained: 0.406 g (71.8% yield). This salt is very hygroscopic an should be kept under Ar atmosphere.

Anal. Calcd for $C_{10}H_{13}Br_2NO$: C, 37.18; H, 4.06; N, 4.33. Found: C, 37.34; H, 4.34; N, 4.37. IR (ν, cm^{-1}): 1728 (ν_{CO}). ^1H NMR (DMSO-d_6, δ): 2.52 (s, 3H, 3-Me, lut), 2.56 (s, 3H, 2-Me, lut), 4.69 (s, 2H, CH_2Br), 5.99 (s, 2H, NCH_2), 7.94 (pseudot, 1H, H_5, lut, $^3J_{HH} = 7.2$), 8.46 (d, 1H, H_4, lut, $^3J_{HH} = 7.6$), 8.66 (d, 1H, H_6, lut, $^3J_{HH} = 6.8$).

Synthesis of 1c. To a suspension of **1b** (0.350 g, 1.08 mmol) in 20 mL of anhydrous THF under Ar atmosphere, an excess of pyridine (3.5 mL, 43 mmol) was added. The resulting mixture was refluxed for 2.5 h and, after cooling, filtered to give **1c** as a pale-brown solid, which was washed with THF (10 mL) and Et_2O (20 mL) and dried in vacuo. Obtained: 0.370 g (84.9% yield).

Anal. Calcd for $C_{15}H_{18}Br_2N_2O$: C, 44.80; H, 4.51; N, 6.96. Found: C, 44.45; H, 4.61; N, 6.80. IR (ν, cm^{-1}): 1747 (ν_{CO}). ^1H NMR (DMSO-d_6, δ): 2.51 (s, 3H, 3-Me, lut), 2.71 (s, 3H, 2-Me, lut), 6.33 (s, 2H, CH_2N, lut), 6.39 (s, 2H, CH_2N, py), 7.97 (dd, 1H, H_5, lut, $^3J_{H5H4} = 7.6$, $^3J_{H5H6} = 6.0$), 8.27 (pseudot, 2H, H_m, py, $^3J_{HH} = 7.2$), 8.48 (d, 1H, H_4, lut, $^3J_{HH} = 7.6$), 8.74 (t, 1H, H_p, py, $^3J_{HH} = 7.6$), 8.95 (d, 1H, H_6, lut, $^3J_{HH} = 6.0$), 9.16 (d, 1H, H_o, py, $^3J_{HH} = 6.8$). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 18.02 (2-Me, lut), 19.82 (3-Me, lut), 64.73 (CH_2N, lut), 66.65 (CH_2N, py), 124.84 (C_5, lut), 128.25 (C_m, py), 138.81, 156.42 (C_2, C_3, lut), 144.59 (C_6, lut), 146.49 (C_o, py), 147.12 (C_4, lut), 147.31 (C_p, py), 194.29 (CO).

Synthesis of 2c. Complex **2c** was prepared following the same method as that reported for **2a**. Thus, **1c** (0.250 g, 0.62 mmol) was refluxed in CH_2Cl_2 (25 mL) with $Pd(OAc)_2$ (0.140 g, 0.62 mmol) to give **2c** as a deep orange solid. Obtained: 0.250 g (79.4% yield)

Anal. Calcd for $C_{15}H_{16}Br_2N_2OPd$: C, 35.57; H, 3.18; N, 5.53. Found: C, 35.94; H, 2.76; N, 5.51. IR (ν, cm^{-1}): 1589 (ν_{CO}, ylide). ^1H NMR (DMSO-d_6, δ): 2.51 (s, 3H, 3-Me, lut), 2.73 (s, broad, 3H, 2-Me, lut), 5.86 (s, 1H, PdC(H)N), 5.91 (s, 1H, PdC(H)N), 7.80 (pseudot, 1H, H_5, lut, $^3J_{HH} = 7.0$), 8.06 (pseudot, 2H, H_m, py, $^3J_{HH} = 6.4$), 8.28 (d, 1H, H_4, lut, $^3J_{HH} = 7.2$), 8.50 (t, 1H, H_p, py, $^3J_{HH} = 7.0$), 9.23 (d, 2H, H_o, py, $^3J_{HH} = 5.8$), 9.51 (s, broad, 1H, H_6, lut). This compound was too insoluble for proper measurement of the ^{13}C NMR, even in DMSO-d_6 and using long accumulation times.

Synthesis of 3c. Complex **3c** was obtained following the same synthetic method as that described for **3a**. Thus, **2c** (0.180 g, 0.355 mmol) was reacted with $AgClO_4$ (0.074 g, 0.355 mmol) and Tl(acac) (0.108 g, 0.355 mmol) in 50 mL of a mixture CH_2Cl_2/acetone (9/1) to give **3c** as a yellow solid. Obtained: 0.120 g (61.9% yield).

Anal. Calcd for $C_{20}H_{23}ClN_2O_7Pd$: C, 44.05; H, 4.25; N, 5.14. Found: C, 43.77; H, 4.10; N, 5.34. IR (ν, cm^{-1}): 1600 (ν_{CO}, ylide), 1578, 1507 (ν_{CO}, acac). ^1H NMR (CD_2Cl_2, δ): 1.88 (s, 3H, Me, acac), 1.94 (s, 3H, Me, acac), 2.58 (s, 3H, 3-Me, lut), 2.82 (s, 3H, 2-Me, lut), 5.41 (s, 1H, CH, acac), 5.68 (s, 1H, PdC(H)N-lut), 5.79 (s, 1H, PdC(H)N-py), 7.64 (dd, 1H, H_5, lut, $^3J_{H5H4} = 7.6$, $^3J_{H5H6} = 5.6$), 7.95 (dd, 2H, H_m, py, $^3J_{HmHp} = 7.6$, $^3J_{HmHo} = 6.4$), 8.16 (d, 1H, H_4, lut, $^3J_{H5H4} = 7.6$), 8.43 (tt, 1H, H_p, py, $^3J_{HpHm} = 7.6$, $^4J_{HpHo} = 1.2$), 9.25 (dd, 2H, H_o, py, $^3J_{HoHm} = 6.4$, $^4J_{HoHp} = 1.2$), 9.45 (dd, 1H, H_6, lut, $^3J_{H6H5} = 5.6$, $^4J_{H6H4} = 0.8$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 17.29 (2-Me, lut), 19.94 (3-Me, lut), 27.44, 27.51 (Me, acac), 65.96 (PdC(H)N-lut), 66.74 (PdC(H)N-py), 100.16 (CH, acac), 123.68 (C_5, lut), 127.12 (C_m, py), 137.67, 155.44 (C_2, C_3, lut), 143.78 (C_p, py), 144.27 (C_6, lut), 144.68 (C_o, py), 144.77 (C_4, lut), 168.08 (CO, ylide), 187.17, 187.59 (CO, acac).

Synthesis of 1d. The bis-isoquinolinium salt **1d** was prepared following a method similar to that described for **1b**. Thus, 1,3-dibromoacetone (0.5 g, 1.621 mmol) was reacted with a large excess of isoquinoline (7.68 mL, 64.85 mmol) in toluene to give **1d** as an orange solid. The yield was quantitative.

Anal. Calcd for $C_{21}H_{18}Br_2N_2O$: C, 53.19; H, 3.83; N, 5.91. Found: C, 52.96; H, 3.77; N, 6.00. IR (ν, cm^{-1}): 1748 (ν_{CO}). ^1H NMR (DMSO-d_6, δ): 6.49 (s, 2H, NCH_2), 8.05 (t, 1H, H_4, $^3J_{HH} =$

7.6), 8.24 (t, 1H, H_5, $^3J_{HH} = 7.6$), 8.36 (d, 1H, H_6), 8.51 (d, 1H, H_3), 8.70 (d, 1H, H_7, $^3J_{H7H8} = 6.8$), 8.88 (d, 1H, H_8), 10.21 (s, 1H, H_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 66.61 (NCH_2), 125.81 (C_7), 127.84 (C_6), 131.00 (C_3), 131.91 (C_4), 136.44 (C_8), 138.07 (C_5), 151.84 (C_2), 127.04, 137.79 (quaternary C atoms), 194.59 (CO).

Synthesis of 2d. Complex **2d** was prepared following the same method as that reported for **2a**. The bis-isoquinolinium salt **1d** (0.500 g, 1.05 mmol) was reacted with $Pd(OAc)_2$ (0.237 g, 1.05 mmol) in refluxing CH_2Cl_2 (25 mL) to give **2d** as a deep orange solid. Obtained: 0.347 g (56.9% yield).

Anal. Calcd for $C_{21}H_{16}Br_2N_2OPd$: C, 43.60; H, 2.79; N, 4.84. Found: C, 43.43; H, 2.69; N, 4.90. IR (ν, cm^{-1}): 1590 (ν_{CO}, ylide). ^1H NMR (DMSO-d_6, δ): 6.12 (s, 1H, PdC(H)N), 8.04 (t, 1H, H_4, $^3J_{HH} = 7.6$), 8.24 (t, 1H, H_5, $^3J_{HH} = 7.2$), 8.31 (d, 1H, H_6), 8.51−8.54 (m, 2H, $H_3 + H_7$), 9.05 (d, 1H, H_8, $^3J_{H7H8} = 6.8$), 10.36 (s, 1H, H_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 73.69 (PdC(H)N), 124.89 (C_7), 127.79 (C_6), 130.51 (C_3), 131.45 (C_4), 135.93 (C_8), 136.79 (C_5), 148.88 (C_2), 127.51, 136.85 (quaternary C atoms), 172.44 (CO).

Synthesis of 3d. Complex **3d** was obtained following the same synthetic method as that described for **3a**. Thus, **2d** (0.200 g, 0.346 mmol) was reacted with $AgClO_4$ (0.072 g, 0.346 mmol) and Tl(acac) (0.105 g, 0.346 mmol) in CH_2Cl_2/acetone (50 mL; 9/1) to give **3d** as a yellow solid. Obtained: 0.155 g (72.6% yield).

Anal. Calcd for $C_{26}H_{23}ClN_2O_7Pd$: C, 50.59; H, 3.75; N, 4.53. Found: C, 50.36; H, 3.50; N, 4.40. IR (ν, cm^{-1}): 1605 (ν_{CO}, ylide), 1567, 1511 (ν_{CO}, acac). ^1H NMR (CD_2Cl_2, δ): 1.89 (s, 6H, Me, acac), 5.39 (s, 1H, CH, acac), 5.82 (s, 2H, PdC(H)N), 7.92 (m, 2H, H_4), 8.09−8.12 (m, 4H, $H_5 + H_6$), 8.21 (d, 2H, H_7, $^3J_{H7H8} = 7.2$), 8.32 (d, 2H, H_3, $^3J_{H3H4} = 8.0$), 8.85 (d, 2H, H_8), 10.19 (s, 2H, H_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 27.43 (Me, acac), 66.50 (PdC(H)N), 100.23 (CH, acac), 124.84 (C_7), 127.71 (C_6), 129.98 (C_3), 131.05 (C_4), 135.82 (C_8), 136.45 (C_5), 148.90 (C_2), 127.69, 136.96 (quaternary C atoms), 168.21 (CO, ylide), 187.36 (CO, acac).

Computational Details. Calculations were performed using the GAUSSIAN98 series of programs.[11] The density functional theory was used with the B3LYP functional.[30] Effective core potentials and their associate double-ζ LANL2DZ basis set were used for the palladium and iodine atoms,[11,31a] and in the case of iodine it was supplemented by a d shell.[31b] The C, O, and F atoms were represented by means of the 6-31G(d) basis set, whereas the 6-31G basis set was employed for the H atoms.[32] All geometry optimizations were full with no restrictions. The reliability of the basis set has been tested in the different conformers of N-ylides **7** and **10**, as representative of 1,6-C−H$\cdots$X (X = O, F) intramolecular interactions. The structures were reoptimized with the 6-31G++(d,p) basis set (BII).[32] Inclusion of diffuse functions and polarization functions at the hydrogen atoms slightly elongates the hydrogen bond distance (from 1.957 to 1.963 Å in **7c**, from 2.045 to 2.058 Å in **10c**, and from 1.980 to 1.996 Å in **10t**). However, we do not observe significant changes in relative energies of the conformers (47.0 versus 45.6 kJ mol^{-1} for **7**, and 18.1 versus 20.6 kJ mol^{-1} for **10**). Stationary points located in the potential energy hypersurface were characterized as true minima through vibrational analysis. The topological properties of the electron density were investigated using the XAIM 1.0 program.[33] Solvent effects were taken into account by means of PCM[34] using standard options. Free energies of solvation were calculated with dichloromethane CH_2Cl_2 ($\epsilon = 8.93$) as solvent, keeping the geometry optimized for gas-phase species.

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